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PATENT SPECIFICATION

975,454

NO DRAWINGS.

975,454



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Nov. 9, 1960. No. 38452/60.

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COMPLETE SPECIFICATION.

Isoprene Production.

PATENTS ACT, 1949

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The following corrections were allowed under Section 78 on 7th November 1967

Page 5, line 39, delete "or 2"

Page 5, line 42, for "3" read "2"

Page 5, line 46, for "4" read "3"

Page 5, line 49, for "5" read "4"

Page 5, line 53, for "6" read "5"

Page 5, line 55, for "7" read "6"

Page 5, line 59, for "8" read "7"

Page 5, line 61, for "9" read "8"

Page 5, line 65, for "10" read "9"

Page 5, line 67, for "11" read "10"

Page 5, line 71, for "12" read "11"

Page 5, line 76, for "13" read "12"

Page 5, line 79, for "14" read "13"

Page 5, line 83, for "15" read "14"

Page 5, line 86, for "16" read "15"

THE PATENT OFFICE,
21st December 1967

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COMPLETE SPECIFICATION.

Isoprene Production.

We, THE GOODYEAR TIRE & RUBBER COMPANY, a Corporation organized under the laws of the State of Ohio, United States of America, with offices at 1144 East Market Street, Akron, Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention is directed to process for the preparation of isoprene. It is more specifically directed to process of preparing isoprene by employing propylene as a starting material.

It is known that isoprene may be produced by several different methods. For example, it is known that the destructive distillation of certain terpene hydrocarbons will produce isoprene; isoprene may also be produced by the dehydrogenation of isopentanes and/or isopentenes; and a process for preparing isoprene from propylene is also known, for instance, United States Patent 2,404,056 describes a process of preparing isoprene by polymerizing propylene by means of alumina-silica type catalyst, liquid phosphoric acid catalyst or phosphoric acid mounted on a carrier such as Kieselguhr, to produce a liquid polymer of propylene which boils between 60° C. to 75° C., selecting a fraction of this polymer boiling between 60° C. and 70° C. and then thermally decomposing or cracking this 60—70° C. fraction to isoprene.

None of these prior art processes produce isoprene of sufficient purity in large enough yields to allow isoprene to be employed to prepare synthetic rubber (polyisoprene) at a price low enough to compete with natural rubber.

It is, therefore, the object of this invention to provide a method of producing relatively pure isoprene. Another object is to provide a

method of producing isoprene at relatively low cost. It is another object of this invention to provide a method of preparing isoprene of high purity at high yields and low cost from propylene. It is another object to provide a method of producing isoprene from propylene which produces isoprene at sufficiently low enough cost to allow the isoprene to be formed into synthetic rubber competitive in price and quality with natural rubber.

The objects of this invention are accomplished by dimerizing propylene to form a dimer of propylene which is substantially all 2-methyl pentene-1, by means of a dimerization catalyst having the general formula $Me(R)_n$ in which Me is one metal selected from the group consisting of beryllium, aluminium, gallium and indium; R is at least one substituent selected from the class consisting of hydrogen, monovalent saturated aliphatic hydrocarbon radicals and monovalent aromatic hydrocarbon radicals and n is the valence of the metal, and subsequently decomposing or cracking this 2-methyl pentene-1 in the presence of bromine and recovering the isoprene thus formed.

The basis of the process of this invention is the discovery that certain specific catalysts may be employed to dimerize propylene to form a propylene dimer which is predominantly 2-methyl pentene-1. (These catalysts will be explained in more detail later). It was found that, when 2-methyl pentene-1 is thermally decomposed or cracked, the resultant products contain little, if any, isoprene; instead, rather substantial yields of isobutylene and ethylene are formed. It has now been found that if 2-methyl pentene-1 is decomposed or cracked in the presence of small amounts of bromine or compounds which produce bromine at the

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cracking conditions employed, rather substantial yields of isoprene may be obtained at the expense of the make of isobutylene and ethylene. Therefore, this invention contemplates a two-step process: first, the formation of 2-methyl pentene-1 by the use of specific catalysts from propylene and, second, the decomposition or cracking of the 2-methyl pentene-1 in the presence of bromine or bromine-producing compounds to produce isoprene.

The first step of the process of this invention, that is the dimerization of propylene to form 2-methyl pentene-1, may be generally carried out in any conventional process usually employed to polymerize olefins so long as the specific organo-metallic compounds are employed as the catalyst. It may be a continuous dimerization or a batchwise dimerization. Autoclaves or tube type reactors may be employed. Generally, the temperature employed in the dimerization may vary, broadly from about 100° C. to about 350° C. with about 180 to about 280° C. being preferred. The pressure employed in this dimerization step may vary broadly from about atmospheric to about 5000 p.s.i.g. with about 200 to 3000 p.s.i.g. being preferred. The times which may be employed to dimerize the propylene may vary broadly from about 1 minute to about 4 hours with about 10 minutes to 1 hour being preferred. It is also desirable to maintain dimerization conditions which are anhydrous and oxygen-free as both oxygen and water are detrimental to the catalyst activity. The amount of catalyst employed in the dimerization step may vary broadly from about 1% by weight to about 100% or more by weight based on the propylene to be dimerized. The propylene may be dimerized in both a batch operation and a continuous operation. When employing batchwise operations, it is usually preferred to employ about 10% to about 50% catalyst by weight and when employing a continuous process, it is usually desirable to employ from about 25 to 100% or more of catalyst by weight. The manner in which this dimerization takes place is not particularly critical and such equipment as autoclaves may be employed for both batch and continuous operations. Other equipment such as tubes or coils may be employed to dimerize on a continuous basis.

The dimerization catalysts employed in the practice of this invention to convert propylene into 2-methyl pentene-1 as is stated above, have the general formula $Me(R)_n$, in which the metal Me may be aluminum, gallium, indium or beryllium and R can be either hydrogen, a monovalent saturated aliphatic radical or a monovalent aromatic radical or mixtures thereof, n is a number representing the valence of the metal Me.

Representative examples of the dimerization above and suitable for dimerizing propylene into 2-methyl pentene-1 are aluminum hydride, aluminum dialkyl hydrides such as aluminum diethyl hydride, aluminum propyl hydride and the like; aluminum alkyls such as aluminum triethyl, aluminum tripropyl, aluminum trihexyl, aluminum triisobutyl and the like; aluminum aryls such as aluminum triphenyl and the like; gallium alkyls such as gallium trimethyl, gallium triethyl and the like; beryllium alkyls such as beryllium diethyl and the like; indium alkyls such as indium trimethyl, indium triethyl and the like; gallium aryls such as gallium triphenyl; beryllium aryls such as beryllium diphenyl; indium aryls such as indium triphenyl and the like. If R represents an alkyl radical in the formula it may be any saturated aliphatic alkyl radical having from 1 to about 20 carbon atoms. Of the dimerization catalyst corresponding to the formula set forth above, it is preferred to employ aluminum alkyls such as aluminum triethyl, aluminum tripropyl, aluminum triisobutyl, aluminum trihexyl, aluminum triheptyl and aluminum trioctyl.

A particularly good catalyst has been found which analyses to be a mixed aluminum trihexyl-tripropyl. It is not known whether this is a mixture of aluminum tripropyl and aluminum trihexyl or whether both types of radicals are on the same aluminum atom such as aluminum dipropyl monohexyl and aluminum dihexyl monopropyl or a mixture of two or more of these aluminum alkyls.

The dimerization step in the process of this invention is further illustrated by the following examples which are intended to be representative rather than restrictive of the practice of this invention. These examples illustrate the continuous dimerization of propylene to 2-methyl pentene-1.

In the following two examples propylene was pumped in liquid form by means of a Hills-McCanna reciprocating pump through $\frac{3}{8}$ inch O.D. high pressure tubing to a point where it was merged with liquid aluminum triisobutyl catalyst, also pumped by means of Hills-McCanna reciprocating pumps.

The separate feed vessels from which both the propylene and catalyst were pumped were stainless steel vessels calibrated in a manner in which the amount of liquid removed from them could be ascertained. Hence, the pump rates could be computed. The propylene stream containing the aluminum triisobutyl was then passed through a $\frac{3}{8}$ inch O.D. $\frac{3}{8}$ inch I.D. stainless steel tubing in the form of a coil placed in a heat transfer bath which acted as a preheater. Then the stream was passed into a reactor

coil of the same type of tubing with a volume of 350 cubic centimeters which was considered to be the reaction zone. This reactor coil was likewise heated by a heat transfer medium.

The product having been quenched was passed into a flash distillation stage where the unreacted propylene and the product or dimer, 2-methyl pentene-1, were flash distilled under pressure from the liquid catalyst which was aluminium trihexyl. The catalyst was then recycled to the catalyst storage tank to be used in subsequent runs.

EXAMPLE 1.

A feed stock containing 97.2% by weight of propylene and 2.8% by weight of propane was fed to this reaction zone described above at a pressure of 3000 p.s.i.g. This feed stream contained 28.2% by volume or 34.2% by weight of aluminium triisobutyl based on the weight of the propylene in the feed stock. This mixture was then heated to 200° C. and pumped at a rate such that it remained in the coil for a period of 15 minutes. This resulted in a conversion of 80.7% with a yield of the product, 2-methyl pentene-1, of 74.7% and a reaction efficiency of 92.7% employing recycle techniques.

EXAMPLE 2.

A feed stock containing 97.2% propylene and 2.8% propane was mixed with aluminium triisobutyl in an amount of 28.8% by volume or 35.0% by weight based on the propylene content of the feed stock at a pressure of 3000 p.s.i.g. and at a rate such that a residence time of 15.3 minutes was maintained in the reaction coil and heated to a temperature of 200° C. This resulted in a conversion of 83.0% with a yield of 2-methyl pentene-1 of 75.1%, with an overall reaction efficiency of 90.5% based on recycle of the unreacted propylene.

The materials which act as catalysts in the dimerization of propylene in the practice of this invention, while they may be introduced into the dimerization zone in the form specifically mentioned above, usually are recovered in the form of aluminium tripropyl. In this regard it is evident that these materials do not act in the manner of true catalysts but, instead, undergo a change during the dimerization reaction and are regenerated in the form of the metal trihexyl which may be employed as a catalyst for succeeding dimerizations.

It can be readily ascertained from the two previous examples that excellent yields of 2-methyl pentene-1 may be obtained by dimerizing propylene in the presence of aluminium triisobutyl. Other comparable results may be obtained employing the general techniques outlined in this application using other specific catalysts and other

reaction conditions, all of which have been generally set forth heretofore. It can also be ascertained that the propylene employed in the practice of this invention does not necessarily have to be a pure propylene feed stock. It is quite often desirable to employ a mixed propylene propane feed stock thereby taking advantage of the relatively low price propylene values in such feed stocks. Depending on the exact conditions employed, it may be advisable at times to use other inert diluents in the dimerization of the propylene. Such diluents may be any saturated hydrocarbon which would not undergo any reaction at the conditions employed in the dimerization step.

The second step of the process of this invention, the cracking of 2-methyl pentene-1 in the presence of bromine, may be carried out in the conventional manner usually employed to crack or decompose olefins. For instance, the temperatures employed in the cracking of 2-methyl pentene-1 have not been found to be particularly critical and may vary widely from about 300 to about 1000° C. However, it is generally preferred to crack 2-methyl pentene-1 in the presence of bromine at temperatures ranging from about 600 to about 700° C. The time that the 2-methyl pentene-1 containing the bromine is present in the cracking zone during the practice of this invention has not been found to be particularly critical and may vary broadly from about 0.001 to about 3 seconds. However, best results are obtained if the time in the cracking zone varies from about 0.05 to about 0.5. These times are referred to as residence times and are usually defined as a time required for 1 mol of incoming gas, whether it be pure 2-methyl pentene-1 or 2-methyl pentene-1 in mixture with some other diluent, to pass through the cracking zone. The 2-methyl pentene-1 in the presence of bromine is fed to the cracking zone or cracking reactor either in a pure form or in mixture with other hydrocarbons. Diluents are usually employed as a heat exchange medium. It is the usual procedure to employ a diluent such as steam. The ratio of diluent, if employed in this invention, to 2-methyl pentene-1 may vary widely from about 0.5 l to about 15 l mols of diluent per mol of 2-methyl pentene-1. If more than about 15 l ratio is employed, the benefits received therefrom no longer offset the loss in economy incurred. It is preferred to employ a diluent/olefin mol ratio of about 2 l to 4 l. The pressures employed in the cracking zone in the practice of this invention may be varied widely from about 10 millimeters of mercury to about 500 p.s.i.g. However, it is preferred that the pressure range from about 125 atmospheric to about 100 p.s.i.g.

The amount of bromine or bromine producing material employed in the practice

of this invention may range from about 0.5 to 50 mol per cent of bromine based on the total mols of 2-methyl pentene-1. It should be understood that this is calculated on the bromine content released from the organic or inorganic bromine producing materials. It is preferred to employ from about 2 to 25 mol per cent. Excellent results have been obtained employing from about 5 to 10 mol per cent. The bromine may be supplied in the practice of this invention as bromine or any organic or inorganic bromine liberating compound, that is any compound which decomposes under the cracking conditions employed to produce bromine. If organic bromine liberating compounds are employed it has been found convenient to use them in the form of a solution and dissolve them in the 2-methyl pentene-1. If inorganic bromine liberating compounds are employed, it has been found convenient to dissolve them in water which is later employed as a diluent in the cracking process. Representative of the organic compounds which produce bromine and may be employed in the practice of this invention are ethyl bromide, 2-bromopropane, 1-bromobutane, 1-bromopropane, alpha bromotoluene, bromobenzene, 1,2-dibromoethane and the like. Representative of the inorganic bromides which may be employed are the water-soluble bromine salts such as ammonium bromide and the like. Of all these compounds useful in the practice of this invention they must decompose or disassociate to form bromine. Bromine gas may be employed as well as any of the organic or inorganic compounds mentioned above. However, when any bromine producing compound is employed in the practice of this invention the bromine is always recovered after passing through the cracking zone in the form of hydrogen bromide. Therefore, it is usually preferred to employ hydrogen bromide in the first instance in the practice of this invention for the reason that hydrogen bromide may be dissolved in the water which is employed to produce steam as the cracking diluent, thus providing a very economical embodiment of this invention where the only bromine-containing compound which need be handled is hydrogen bromide.

The practice of the second step in the process of this invention is illustrated by the following experiments which are representative and not to be considered restrictive.

EXAMPLE 3.

All of the decomposition experiments were performed in the cracking assembly consisting of a "hairpin" coil prepared from

$\frac{1}{2}$ inch O.D. Type 316 stainless steel tubing. This cracking coil was immersed in a bed of fluidized heat transfer powder which was a microspheroidal alumina silica material normally employed as a cracking catalyst in cracking crude oil stocks. This heat transfer powder was heated both by electrical resistance heaters and by combusting a natural gas/air flame directly in the fluidized powder bed. The temperature gradient from top to bottom of the bed and from the bed to the cracking coil was never more than from about 5 to 6° C. Temperatures within the cracking zone and in the fluidized bed were obtained by conventional thermocouple procedures. The procedure employed was to bring the heat transfer powder up to about 500° C. by employing the electrical resistance heaters while the bed was being fluidized by means of air jets; then a direct natural gas/air flame was employed to bring the bed up to the desired cracking or operating temperatures. The 2-methyl pentene-1 was mixed with the bromine or the bromine-producing material in the desired amounts prior to its being passed through the cracking zone. Water and the 2-methyl pentene-1 containing the bromine were pumped at the proper rates necessary to produce the desired steam to hydrocarbon ratios and to give the desired residence time of the 2-methyl pentene-1 in the cracking zone. When all variables had been adjusted to the desired operating conditions, the products were collected by means of cooled receivers, if liquid; if gas, they were metered at atmospheric pressures and room temperature conditions. Products were collected and analyzed for content and yield by conventional analytical methods. Conventional recycle techniques were employed to obtain ultimate yields and reaction efficiencies. The pressure employed was about 1 pound per square inch gauge.

Each individual run is reported in Table 1 below as the run number; the temperature of each experiment is reported in column 2 in °C.; the residence time within the cracking zone is reported in seconds in column 3; the bromine containing compound, if any, is listed in column 4; the amount of bromine-containing compound is reported in mol per cent, based on the 2-methyl pentene-1, in column 5; the yield of isoprene per pass in mol per cent of 2-methyl pentene-1 is reported in column 6 and the overall reaction efficiency is reported in terms of isoprene produced per mol of 2-methyl pentene-1 employing conventional recycle techniques in column 7.

TABLE I.

Run No.	Temperature °C.	Residence Time- Seconds	Bromine Compound	Amount Bromine Compound	Yield Per Pass	Reaction Efficiency
5						
156 HA	675.3	0.2802	—	None (Control)	4.38	13.08
250 H	676.2	0.3340	HBR	6.84	32.77	43.72
191 H	646.6	0.2688	—	None (Control)	1.87	34.32
10 245 HA	659.3	0.3542	HBR	6.47	34.25	49.80
246 H	659.8	0.2400	HBR	6.18	24.38	47.00
251 HA	652.2	0.3600	HBR	5.21	30.42	43.10

It can be ascertained from the table above that very substantial yields of isoprene per pass may be obtained by decomposing 2-methyl pentene-1 in the presence of HBr. It should also be noted that very good reaction efficiencies are obtained when conventional recycle techniques are employed. Other comparable results may also be obtained employing other reaction conditions and other bromine-producing compounds, all being in accordance with the teachings set forth in this application.

25 WHAT WE CLAIM IS:—

1. A method of preparing isoprene which includes dimerizing propylene by means of a catalyst of the formula $Me(R)_n$ in which Me is one metal selected from beryllium, aluminium, gallium, or indium; R is at least one substituent selected from hydrogen, monovalent saturated aliphatic hydrocarbon radicals or monovalent aromatic hydrocarbon radicals; and n is the valence of the metal Me to obtain 2-methyl pentene-1, subsequently cracking 2-methyl pentene-1 in the presence of bromine to form isoprene and collecting the isoprene thus formed.

2. A method according to Claim 1 or 2, in which the dimerization is carried out at a temperature of from 100° to 350° C.

3. A method according to Claim 3 in which the temperature is of from 180° to 230° C.

4. A method according to any of Claims 1 to 4 in which the dimerization is carried out at a pressure of from atmospheric to 5000 p.s.i.g.

5. A method according to Claim 5 in which the pressure is of from 200 to 3000 p.s.i.g.

6. A method according to any of Claims 1 to 8 in which the dimerization catalyst is an aluminium alkyl.

7. A method according to Claim 7 in

which the aluminium alkyl is aluminium triisopropyl and or aluminium trihexyl.

8. A method according to any of Claims 1 to 8 in which the bromine is supplied in the form of a bromine producing compound. 60

9. A method according to Claim 9 in which the bromine producing compound is hydrogen bromide.

10. A method according to any of Claims 1 to 10 in which the cracking is carried out at a temperature of from 300° to 1000° C. 65

11. A method according to Claim 11 in which the temperature is of from 600° to 700° C.

12. A method according to any of Claims 1 to 12 in which 2-methyl pentene-1 is fed to the cracking zone in a pure form, in mixture with other hydrocarbons or with a diluent. 70

13. A method according to any of Claims 1 to 13 in which the cracking is carried out at a pressure of from 10 millimeters of mercury to 500 p.s.i.g. 75

14. A method according to Claim 14 in which the pressure is of from atmospheric to 100 p.s.i.g. 80

15. A method according to any of Claims 1 to 15 in which the bromine employed is from 0.5 to 50 mol per cent based on the total mols of 2-methyl pentene-1. 85

16. A method according to Claim 16 in which the mol per cent is of from 2 to 25.

17. A method of preparing isoprene comprising dimerizing propylene to form 2-methyl pentene-1, subsequently decomposing the 2-methyl pentene-1 to isoprene, in which the dimerization takes place at a temperature ranging from 180 to 230° C. in the presence of at least one catalyst selected from aluminium tripropyl, aluminium trihexyl, aluminium dipropyl monohexyl or aluminium dihexyl monopropyl, and in which the decomposition takes place at a temperature ranging from 600 to 700° C., 90

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- in the presence of from about 5 to 10 mol per cent hydrogen bromide based on the total mols of 2-methyl pentane-1, employing steam as a diluent at a mol ratio of steam to 2-methyl pentane-1 of 2 to 1 to 4 to 1.
18. A method of preparing isoprene from propylene substantially as set forth and described hereinbefore.
19. Isoprene when prepared according to the method of any of the preceding claims.
20. Isoprene when prepared by cracking 2-methyl pentane-1 in the presence of bromine.

MARKS & CLERK.

Reference has been directed in pursuance of Section 9, subsection (1) of the Patents Act, 1949, to Patent Nos. 868566 and 831,249.

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